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RADIATION CHEMISTRY LABORATORY SERIES

RESEARCH REPORT NO. 6

IRRADIATION "FACTOR-DEPENDENCY"

Some Vinyl Monomers: Degassing and Irradiation Cycle

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QUARTERMASTER RESEARCH & ENGINEERING CENTER

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FOREWORD

This report, Research Report No. 6, in the Irradiation "Factor-Dependency" series of the Radiation Chemistry Laboratory, deals with the concurrent effect of (a) degassing, and (b) irradiation cycle, on the irradiation-induced polymerization of eight monomer systems.

Data of Research Report No. 1, Styrene, indicate that factors such as atmosphere, degassing, diluent, dose, dose rate, moisture, and temperature all appear to be important parameters. Atmosphere, dose rate, and temperature were found to be statistically significant, with variations in dose rate being approximately twice as effective as variations in either atmosphere or temperature. With respect to molecular weight, temperature was found to be statistically significant at dose rates of 25,000, 50,000, and 100,000 rads per exposure. The non-additivity of dose was reported.

Research Report No. 2, Some Vinyl Monomers, gave results which indicate that under the experimental conditions employed: (1) polymerization rate is not equal to $kI^{\frac{1}{2}}$, (2) the E-value ("G_e"-value or amount of polymer obtained per unit of radiation energy) decreases with an increase in dose rate, (3) there is a non-additivity of dose, and (4) unless parameters are critically defined, the formulation of reaction rate has no significance.

Research Report No. 3, Styrene with Additives, provided data from which it was concluded for the additives used that: (1) the effect of an additive is a function of dose rate with respect to both molecular weight and yield of polymer, (2) the molecular weight decreases with an increase in dose rate for all additives used, (3) there appears to be an inverse ratio with respect to molecular weight and yield, (4) an additive, as a function of dose rate, may either decrease or increase the yield of polymer, and (5) the efficiency of polymerization decreases markedly at the higher dose rates used in these studies.

From Research Report No. 4, Irradiation Cycle, it was concluded that: (1) a cycle of something more than three minutes at 75°C is the most efficient for the irradiation-induced polymerization of certain vinyl monomers, (2) the better relative efficiency of a time cycle over continuous irradiation decreases with an increase in dose rate, (3) efficiency decreases markedly at the higher dose rates used in these studies, (4) reaction rate formulations, derived under experimental conditions different from those used in this study, are not applicable, and (5) the most desirable time cycle and temperature are functions of the monomer system.

Research Report No. 5, Degassing, presented experimental results from which it was concluded that: (1) degassing may significantly increase the yield of polymer obtained by the irradiation-induced polymerization of vinyl monomers, and (2) the relative importance of degassing is interdependent on (a) the monomer system, (b) the dose rate, and (c) in certain cases at least, the presence of an inert atmosphere such as argon.

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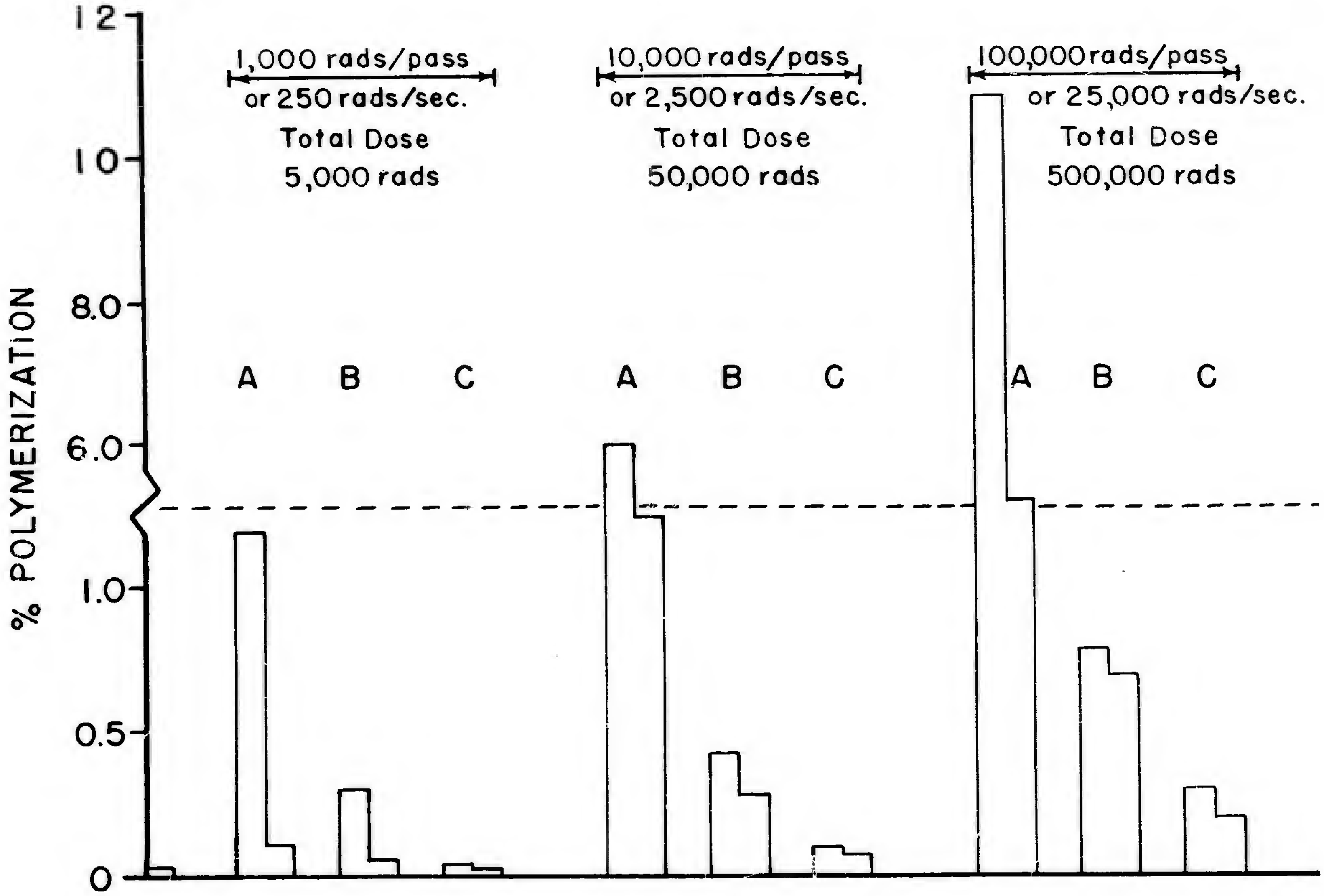

Figure 1. Acrylonitrile (D-682): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. The sample for the left member of each pair was degassed once. Comparable heat-control value is shown in the lower-left corner.

Irradiation "Factor-Dependency": Degassing and Irradiation Cycle

By Ed. F. Degering, G. J. Caldarella, Flora E. Evans, and Stephen Grib

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A. Introduction

The experimental results reported herein and heretofore represent relative rather than absolute values. This is a consequence of certain slight uncontrollable variations in parameters, which were considered in some detail in Section A of Research Reports No. 3 and 4 of the Radiation Chemistry Laboratory Series.

In Research Report No. 4 consideration was given to the irradiation cycle and in Research Report No. 5 results were given relative to the effect of degassing monomer systems prior to irradiation. In this report the combined effect of the irradiation cycle and degassing are considered.

B. Preparation of Samples

The meticulous procedure developed in the Radiation Chemistry Laboratory for the preparation of samples for irradiation was considered in some detail in Section B of Research Reports No. 4 and 5 of the Radiation Chemistry Laboratory Series. Samples for this study were evacuated to about 10 microns at -195°C and then sealed off.

The monomer systems used in this study were acrylonitrile, butyl acrylate, styrene, vinyl acetate, acrylonitrile-styrene (1/1 mixture by volume), butyl acrylate-styrene (1/1), and vinyl acetate-styrene (1/1). Nine sets of samples were prepared in triplicate for these monomer systems. Two samples of each set were degassed once whereas the third sample was not degassed.

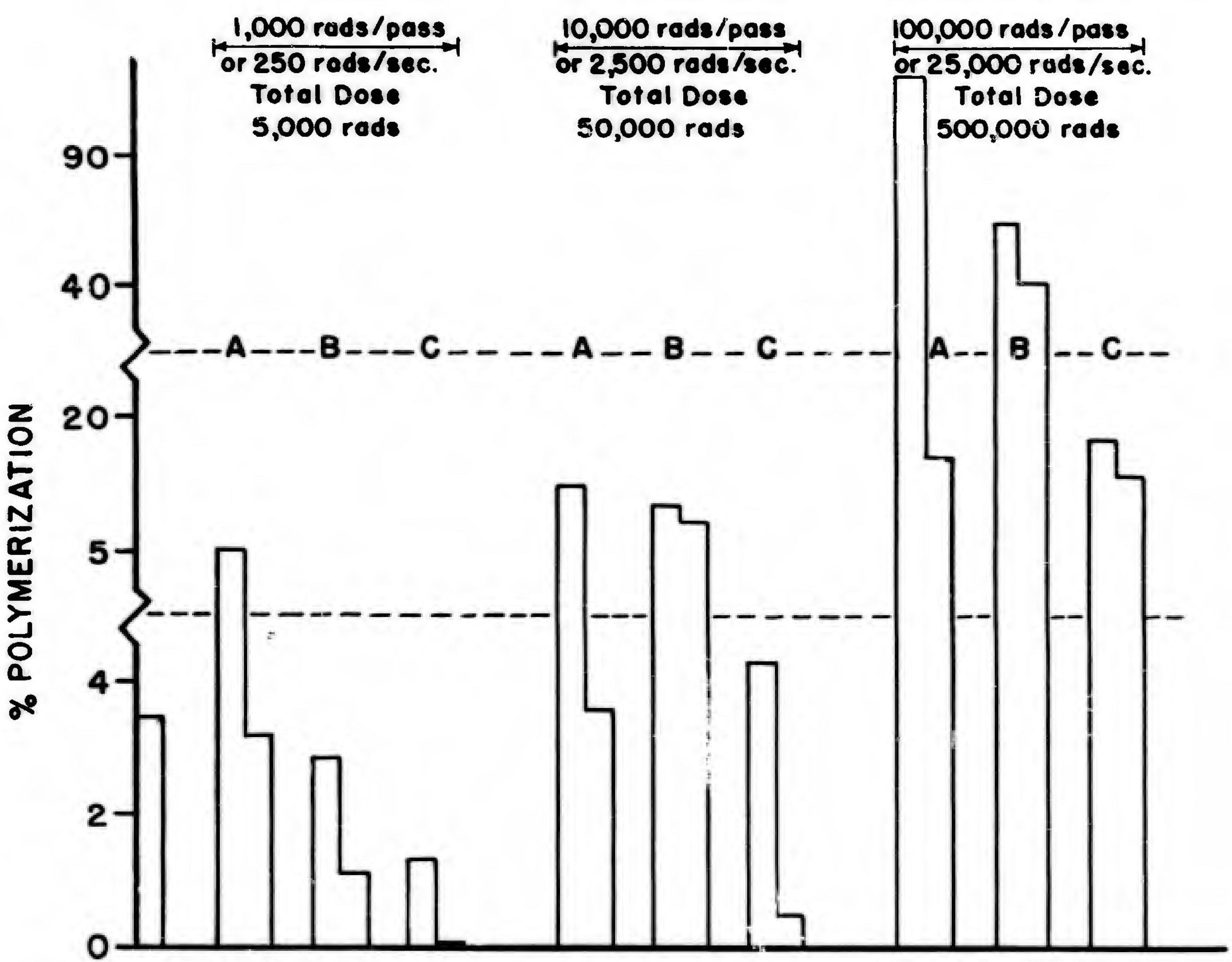

Figure 2. Butyl Acrylate (D-683): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. The sample for the left member of each pair was degassed once. Comparable heat-control value is shown in the lower-left corner. The samples for the A-bars, however, received only one-fifth of the total dose indicated.

C. Irradiation of Samples

Three irradiation procedures were used, which are designated on the bar graphs as A, B, and C. In the A-procedure, the samples were pre-heated at 75°C for forty-five minutes, then given one exposure at the desired dose rate and returned to the oven for a forty-five-minute heating period. Five such irradiation and heating cycles were used for each of the monomer systems except butyl acrylate, which was given only one complete cycle.

In the B-procedure, the samples were irradiated on a shuttle at 25°C at intervals of one-half, one, and three minutes, at the same dose rate as the samples in the A-procedure. The butyl acrylate samples, however, received five times the irradiation by this procedure as they did by use of the A-procedure. The irradiation by the A- and B-procedures was accomplished by use of a 1.5 Mev electron accelerator (High Voltage Engineering Corporation) operating at 2 Mev.

In the C-procedure, the samples were subjected to continuous irradiation at 25°C by use of a 2 Mev Resonant Transformer (General Electric Company) at the desired dose rate until they had received the same dose as the comparable samples which were irradiated by the A- and B-procedures.

D. Processing of Samples

Irradiated monomer systems were processed according to the procedure detailed in Research Report No. 3, Section D (November 1960), and in Research Report No. 4, Section D (December 1960).

E. Experimental Results

1. Acrylonitrile:

The per cent yield of polymer obtained by the irradiation-induced polymerization of acrylonitrile at three different dose

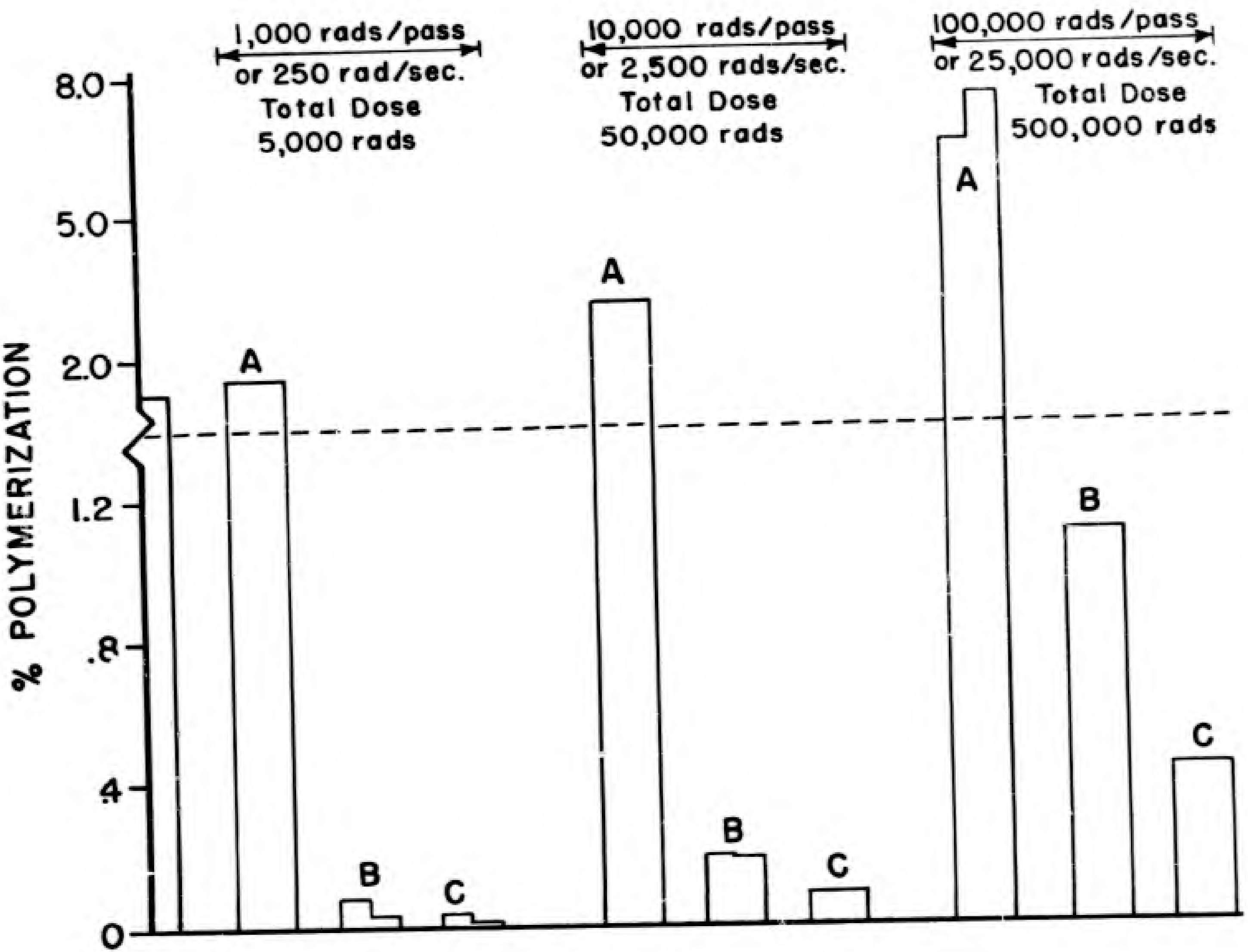

Figure 3. Styrene (D-684): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. The sample for the left member of each pair was degassed once. Comparable heat-control value is shown in the lower-left corner.

rates and dose levels, by use of the A-, B-, and C-procedures, is shown in Figure 1 (page iv). The left bar of each bar-pair represents the average for two degassed samples whereas the right bar of each pair of bars indicates the value obtained for the comparable non-degassed sample. This same system for indicating degassing applies to all of the bar graphs of this report.

The A-procedure (forty-five-minute cycle at 75°C) gives higher yields of polymer at the three dose rates and dose levels than does the B-procedure (one-half- to three-minute cycle at 25°C), and the B-procedure in turn gives higher yields than does the C-procedure (continuous irradiation at 25°C). The heat-control value shown in the lower left of the graph indicates that the heat effect does not account for the large differences between the values obtained by use of the A-procedure and the B- and C-procedures, — unless there is a decided synergistic effect. It seems apparent, therefore, that something more than a three-minute cycle is generally required for optimal yields unless there is a very pronounced synergistic effect when heat and irradiation are combined. The facility used did not lend itself readily to the use of a B-type procedure at 75°C.

The difference in the values obtained by the B- and C-procedures for these seven monomer systems is attributed to the use of intermittent (B-procedure) irradiation in contrast to the continuous irradiation used in the C-procedure, and not to variations in instrumentation, that is, a continuous scanned beam (B-procedure) versus a pulsed circular beam (C-procedure).

The B-bars at the three dose rates are the average values obtained from a half-, one-, and three-minute cycle. There did not appear to be a significant difference between these three short cycles, hence the results were averaged.

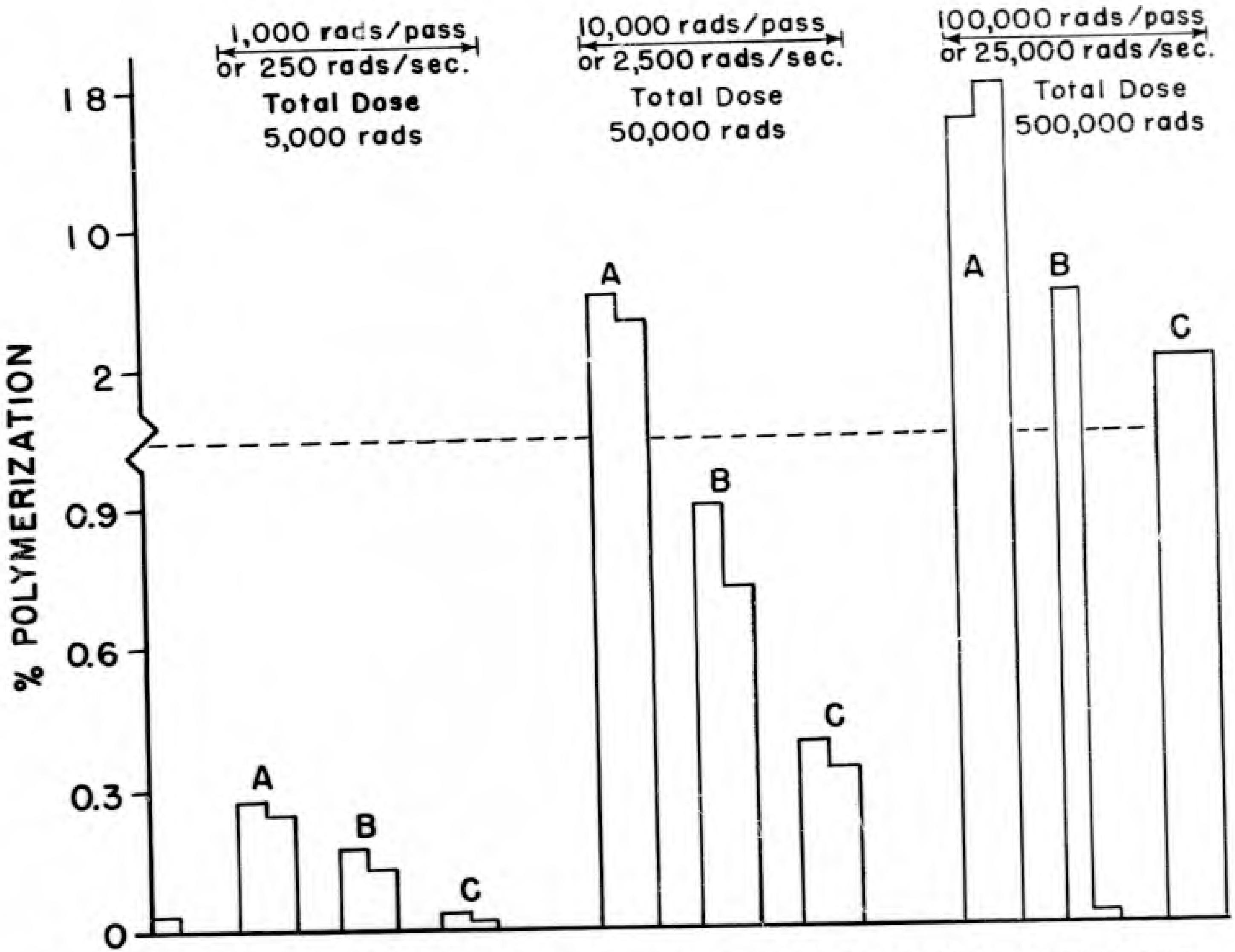

Figure 4. Vinyl Acetate (D-685): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. The sample for the left member of each pair was degassed once. Comparable heat-control value is shown in the lower-left corner.

2. Butyl Acrylate:

The results obtained for the irradiation of butyl acrylate by use of the A-, B-, and C-procedures at the three dose rates are given as Figure 2 (page 2). It should be indicated again, however, that the samples for the B- and C-bars at all three dose rates received five times the dose as that given to the corresponding samples for the A-bars. The A-bars, nonetheless, are consistently higher for each of the dose rates than are the B- and C-bars. The B-bars, similarly, are higher for each of the dose rates than are the corresponding C-bars.

The heat-control value shown by the single bar at the left is for a sample which was exposed to five heating cycles whereas each of the A-samples had only one heating cycle. If the heat polymerization is linear with time, then the heat-control value should be about 0.7% instead of 3.5%. This will be checked as opportunity permits.

Three samples, which were degassed three times, were irradiated at 1,000 rads per exposure on a forty-five-minute cycle at 25°C for a total dose of 5,000 rads in order to compare with the corresponding B- and C-values. The value obtained was 6.2% polymerization, whereas the comparable B-value was 2.9% and the C-value 1.3%. This value of 6.2% obtained by use of a forty-five-minute cycle at 25°C for a dose of 5,000 rads should be contrasted, however, with a value of 5.2% for a dose of 1,000 rads on a forty-five-minute cycle at 75°C. It is apparent, here as in the case of acrylonitrile, that a cycle of more than three minutes at 75°C is required for optimal polymerization per unit of irradiation energy.

3. Styrene:

The data obtained from the irradiation-induced polymerization of styrene at three dose rates and three dose levels by use of the A-, B-, and C-procedures are shown in Figure 3 (page 4).

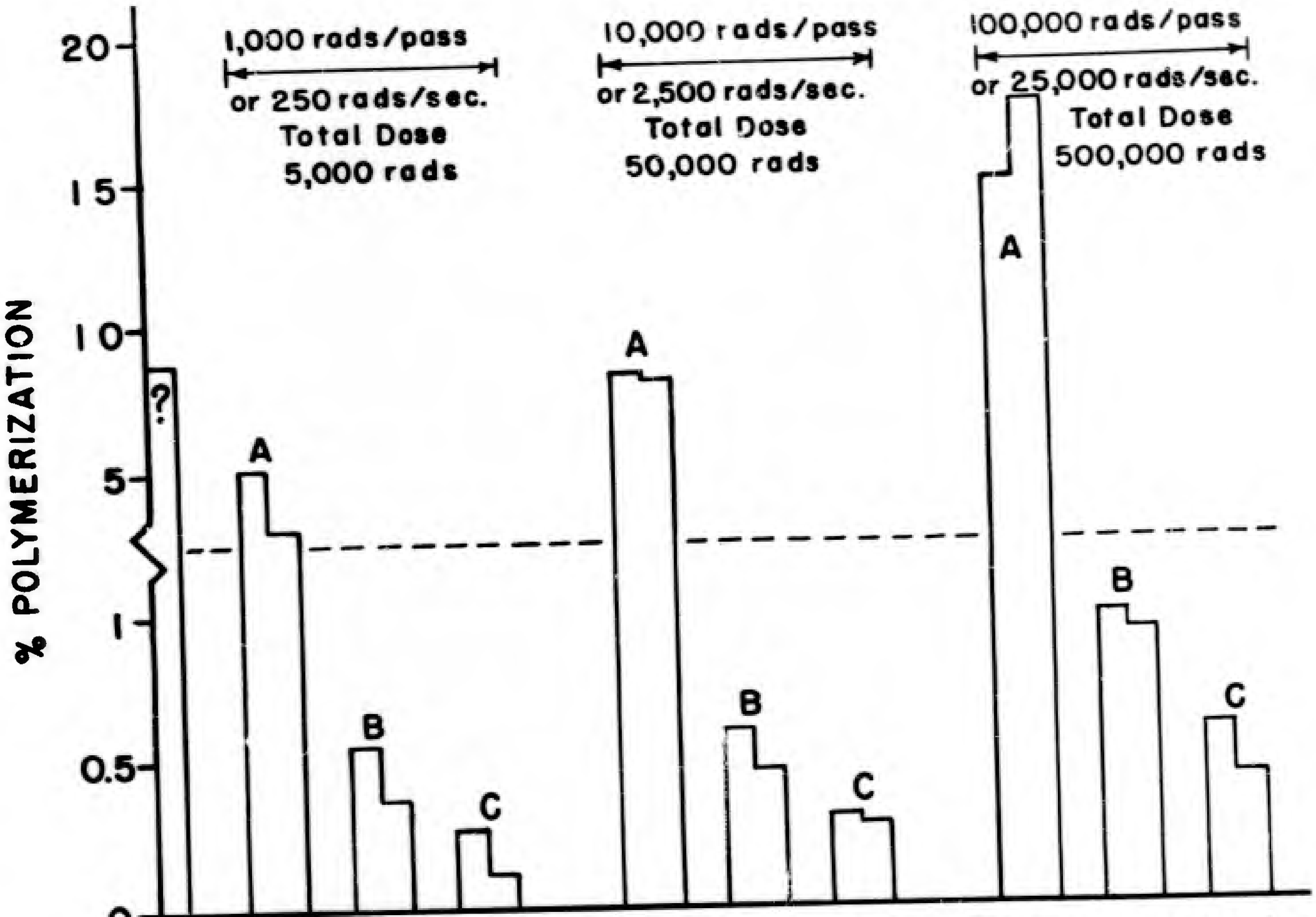

Figure 5. Acrylonitrile-Styrene (1/1 mixture by volume, D-686): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. The sample for the left member of each pair was degassed once. Comparable heat-control value is shown in the lower-left corner.

The A-bars are consistently higher at each dose rate than are the comparable B-bars, and the B-bars in turn are higher at each dose rate than are the comparable C-bars. The heat-control value at the left of the graph is about the same as that for the A-bar at 1,000 rads per exposure. This effect has been encountered in other studies on styrene, and will be investigated more fully. At this low dose rate there appears to be a complex situation, which may result from the involvement of two types of somewhat antagonistic mechanism.

A value of 1.4% polymerization was obtained at a dose rate of 100,000 rads per exposure for a dose of 500,000 rads on a forty-five-minute cycle at 25°C. The corresponding values for the one-half to three-minute cycles (B-procedure) and the continuous irradiation (C-procedure) are respectively 1.1% and 0.5%. The comparable value for the forty-five-minute cycle at 75°C for five exposures is 6.5%. As in the case of acrylonitrile and butyl acrylate, it seems from these results that something more than a three-minute cycle at 75°C is required for optimal irradiation-induced polymerization of styrene per unit of radiation energy.

Degassing has little or no effect on the irradiation-induced polymerization of styrene with the parameters used in this specific study (Figure 3, page 4). Under a different set of parameters, however, the degassing of styrene monomer prior to irradiation was effective in increasing the yield of polymer (cf. Figure 15, page 20, of Research Report No. 5, January, 1961, of this series).

It should be noted also that five exposures of styrene at 1,000 rads each in this study gave 1.8% polymerization, whereas five exposures at 10,000 rads gave only 3.0%, and five exposures at 100,000 rads yielded only 6.5% polymer. Under these conditions only 3.6 times as much polymer was obtained with one hundred times as much energy at the higher dose rate as was produced at the lower dose rate.

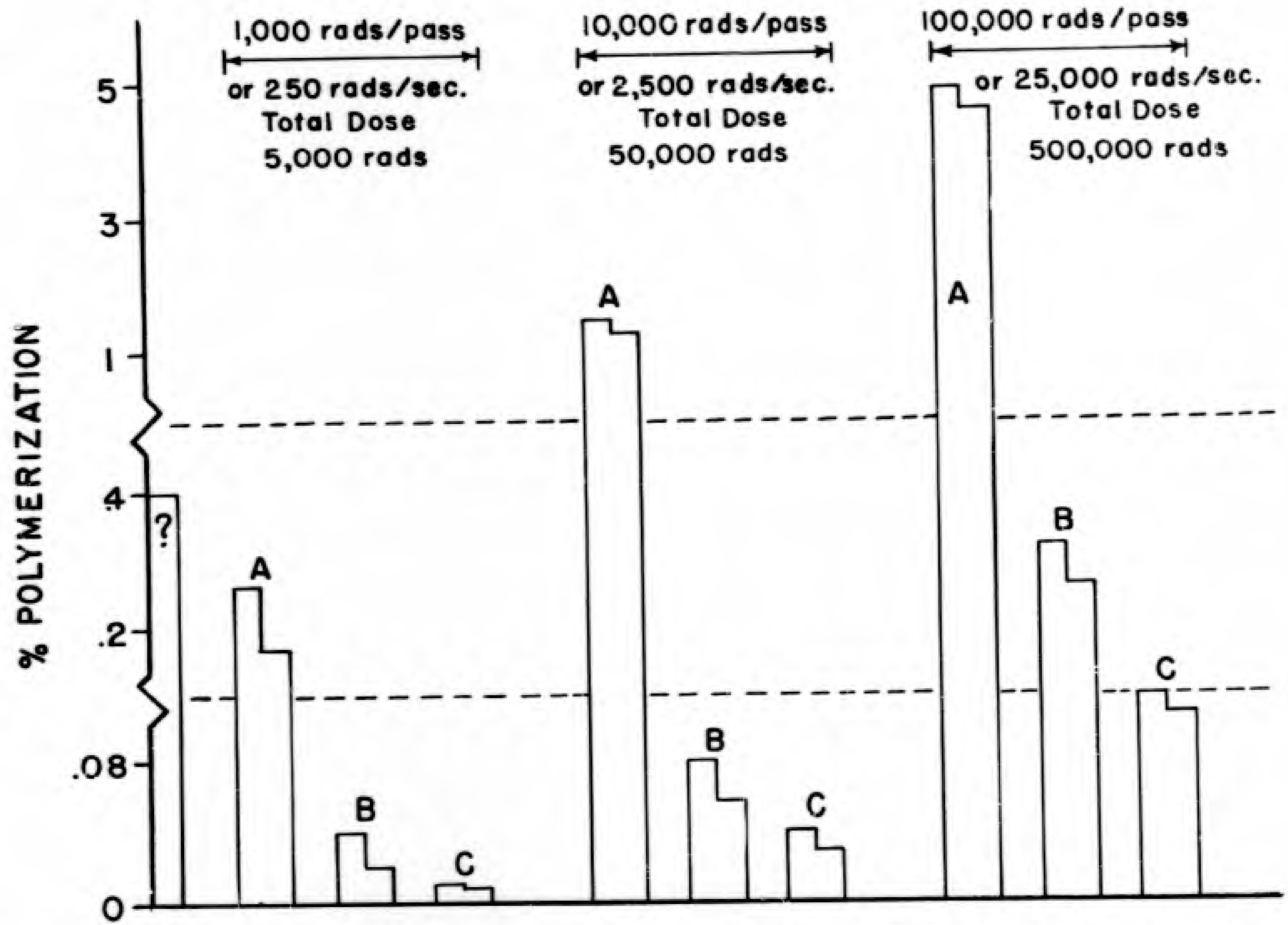

Figure 6. Butyl Acrylate-Styrene (1/1 mixture by volume, D-687): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. The sample for the left member of each pair was degassed once. Comparable heat-control value is shown in the lower-left corner.

4. Vinyl Acetate:

Results obtained for the irradiation-induced polymerization of vinyl acetate by the three procedures at three dose rates, using degassed and non-degassed samples, are shown as Figure 4 (page 6). The A, B, and C designations, as well as the twin bars, convey the same meaning as in the previous discussions.

The values for the A-bars for the three dose rates (A-procedure) are consistently higher than are the values for the B-bars (B-procedure). Similarly, the B-bars are consistently higher than are the C-bars, which represent data obtained by use of the C-procedure. It is evident, therefore, that the use of a forty-five-minute irradiation cycle at 75°C gives higher yields of polyvinyl acetate than does a one-half- to three-minute cycle at 25°C, and that the use of a one-half- to three-minute cycle at 25°C results in higher yields than those obtained by continuous irradiation at 25°C, other factors being comparable.

Samples which were irradiated on a forty-five-minute cycle at 25°C at a dose rate of 10,000 rads per exposure and to a total dose of 50,000 rads, gave an average yield of 1.4% polymer, whereas the corresponding value for comparable results from a one-half- to three-minute cycle is 0.7% and that for continuous irradiation is 0.3%. The comparable value obtained on a forty-five-minute cycle at 75°C for a dose of 50,000 rads is 4.0%. This confirms previous interpretations of experimental data, which led to the conclusion that something more than a three-minute cycle is required for optimal polymerization of vinyl monomers under the conditions of these experiments.

Degassing does not appear to be a very important parameter for the irradiation-induced polymerization of vinyl acetate under the conditions of this study. With another set of parameters, however, in which a degassed sample of freshly distilled vinyl acetate, under 630 mm. of argon, was given five exposures

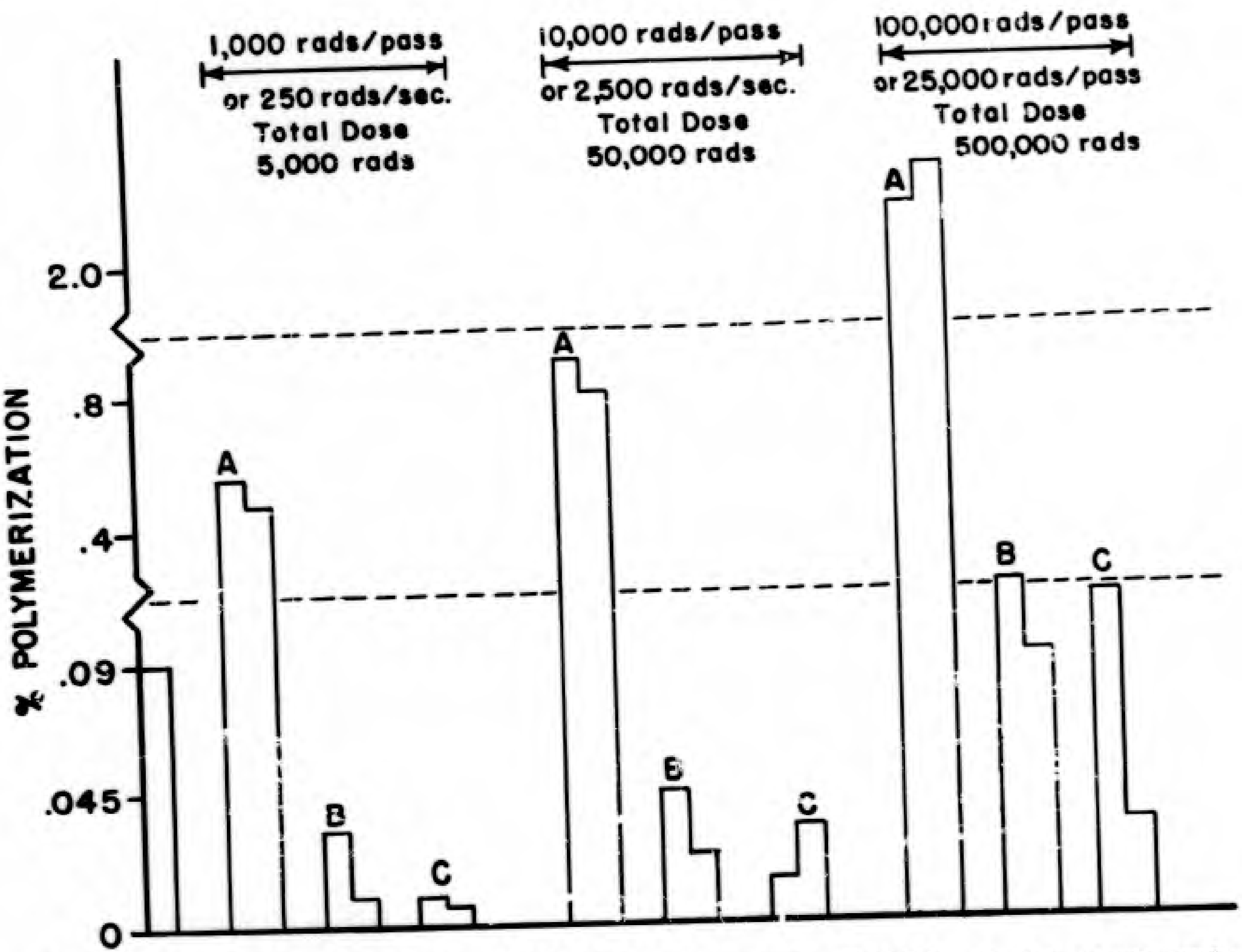

Figure 7. Vinyl Acetate-Styrene (1/1 mixture by volume, D-688): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. The sample for the left member of each pair was degassed once. Comparable heat-control value is shown in the lower-left corner.

at 1,000 rads on a thirty-minute cycle and compared with a non-degassed sample, the respective values obtained were 2.8% and 0.0% (cf. Figure 14, Research Report No. 5, January, 1961, of the Radiation Chemistry Laboratory Series).

5. Acrylonitrile-Styrene (1/1 mixture by volume):

The results obtained for a one-to-one mixture by volume of acrylonitrile and styrene for the three irradiation cycles at the three dose rates and three dose levels are recorded as Figure 5 (page 8). In every case the A-bars of values obtained on the forty-five-minute cycle at 75°C are higher at the three dose rates than are the corresponding B-bars which represent values obtained on a one-half- to three-minute cycle at 25°C. The B-bars in turn are higher than are the corresponding C-bars, which are for values obtained by continuous irradiation.

The effect of degassing is much less apparent in this mixture than it is in the case of acrylonitrile (cf. Figure 1, page iv), yet more apparent than in the case of styrene (cf. Figure 3, page 4). The styrene in this mixture appears to be dominant, as evidenced by both the abnormal heat control and the relatively small degassing effect.

6. Butyl Acrylate-Styrene (1/1 mixture by volume):

The polymerization data obtained for a one-to-one mixture by volume of butyl acrylate and styrene for the three irradiation cycles at the three dose rates and three dose levels are recorded by the bar graphs of Figure 6 (page 10). The A-bars are for values obtained on a forty-five-minute cycle at 75°C which are consistently higher, for the three dose rates and three dose levels, than are the corresponding B-bars for values obtained at 25°C on a one-half- to three-minute cycle. The B-bars in turn are higher than the corresponding C-bars (continuous irradiation at 25°C). Again it seems apparent that a cycle of more than three minutes at 75°C is desirable for optimal yields of polymer.

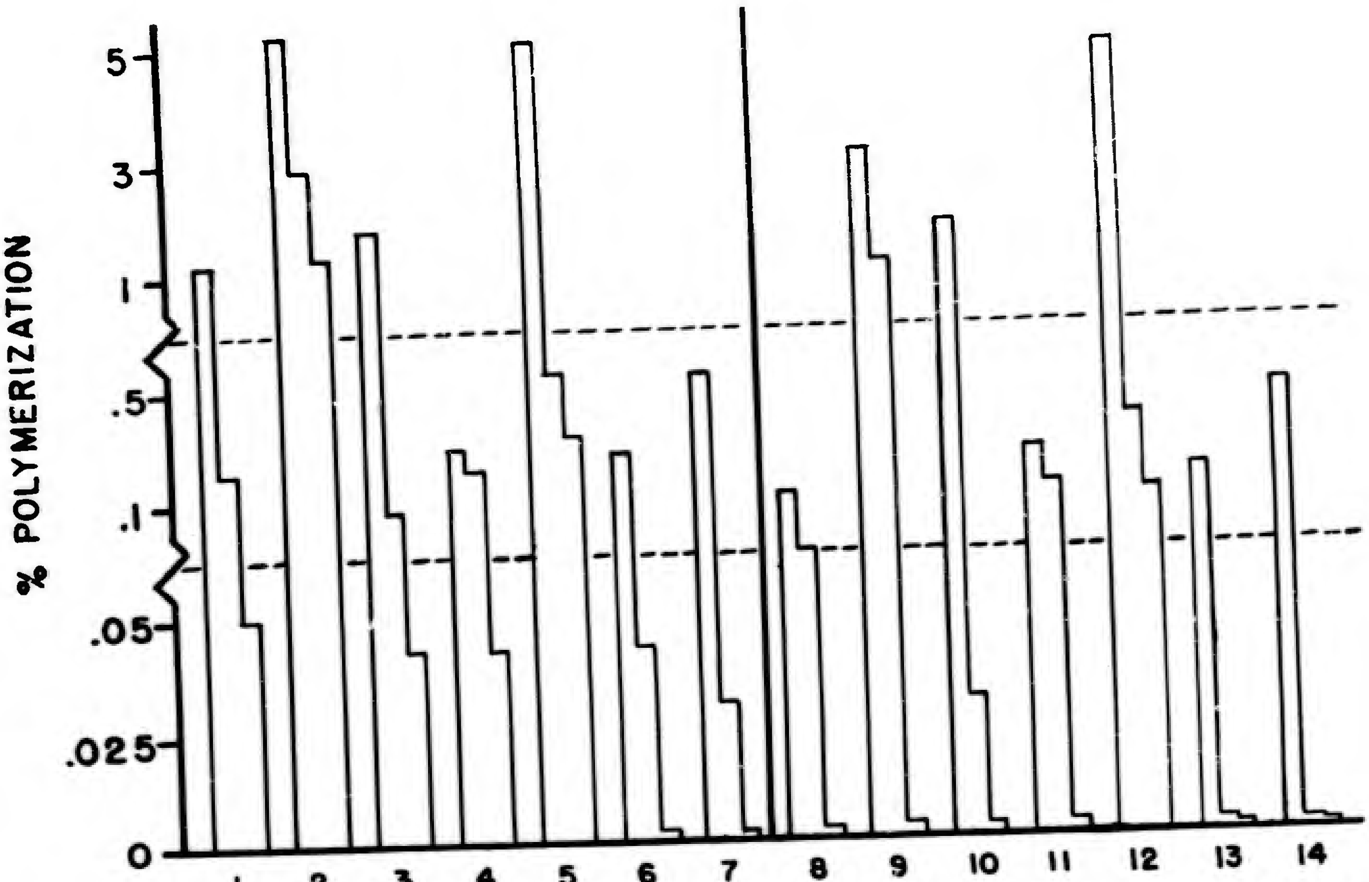

Figure 8. 1,8. Acrylonitrile (D-682); 2,9. Butyl Acrylate (D-683); 3,10. Styrene (D-684); 4,11. Vinyl Acetate (D-685); 5,12. Acrylonitrile-Styrene (1/1, D-686); 6,13. Butyl Acrylate-Styrene (1/1, D-687); and 7,14. Vinyl Acetate-Styrene (1/1, D-688). Samples for the left half of chart were degassed once; the others were not. The left member of each triplet bar-graph was on a 45-minute cycle at 75°C, the center one on a 1/2- to 3-minute cycle at 25°C, and the right member is from continuous irradiation at 25°C. Dose rate: 1,000 rads per exposure or 250 rads per second. Dose: 5,000 rads.

The effect of degassing is less pronounced than in the case of butyl acrylate (cf. Figure 2, page 2), but more apparent than in the case of styrene. The relatively high value for the heat control and the obscuring of the degassing effect, seem to indicate that styrene is the dominant monomer of this mixture.

7. Vinyl Acetate-Styrene (1/1 mixture by volume):

The results for the irradiation-induced polymerization of vinyl acetate and an equal volume of styrene by the three procedures at the three dose rates and three dose levels, are shown as Figure 7 (page 12). The A-bars (forty-five-minute cycle at 75°C) for the three dose rates and three dose levels, are consistently higher than are the corresponding B-bars (one-half- to three-minute cycle at 25°C). The B-bars likewise are consistently higher than are the corresponding C-bars, which represent data obtained by continuous irradiation at 25°C. In this system, once again, styrene appears to be the dominant monomer.

8. Composite Summary of Figures 1 to 7:

Figures 8, 9, and 10 (pages 14, 16, and 18) present a summary by dose rate of the composite effect of the irradiation cycle and degassing on the seven monomer systems of this study. Left to right, the members of the triplet bars represent the results obtained by use of the A-procedure, the B-procedure, and the C-procedure. The bars to the left of center of each figure represent data obtained from samples which were subjected to a single degassing, whereas the values indicated by the bars to the right of each figure are for samples which were not degassed.

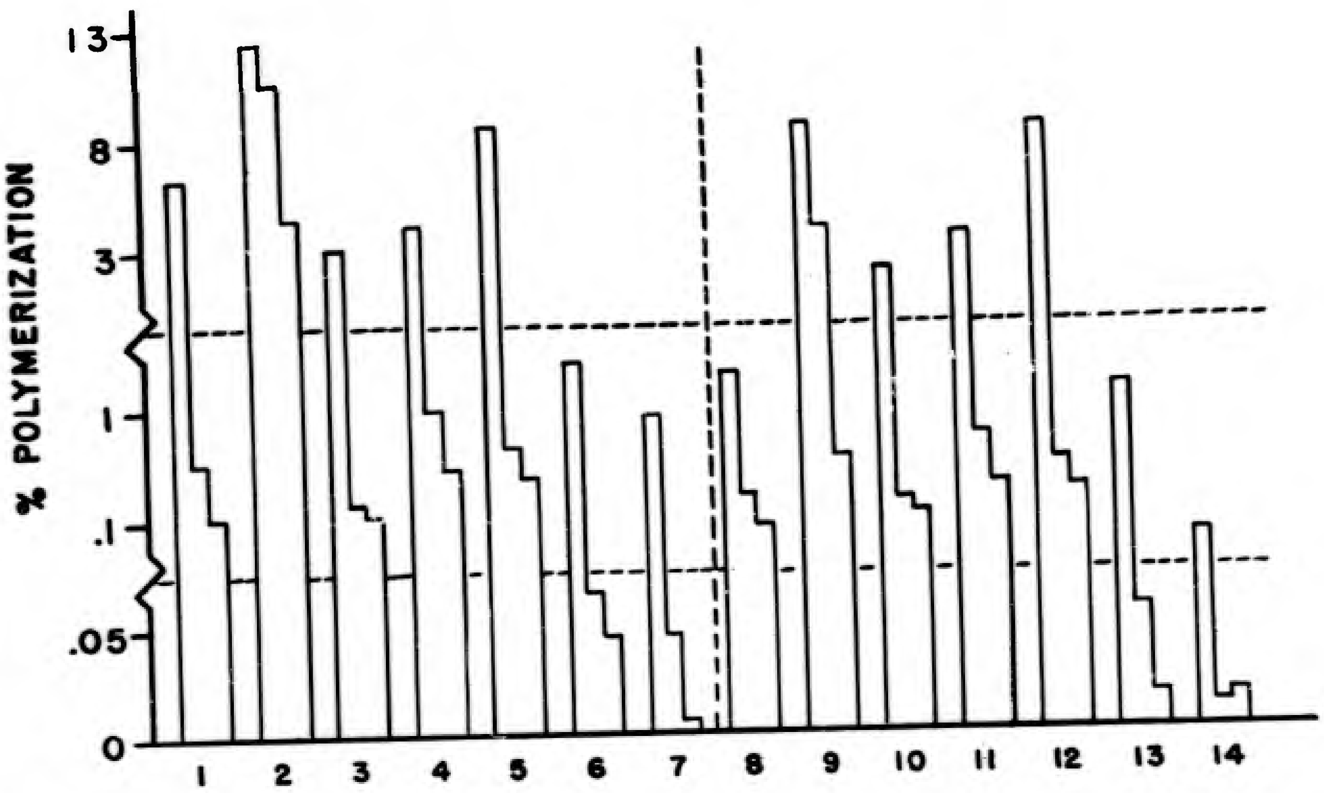

Figure 9. 1, 8. Acrylonitrile (D-682); 2, 9. Butyl Acrylate (D-683); 3, 10. Styrene (D-684); 4, 11. Vinyl Acetate (D-685); 5, 12. Acrylonitrile-Styrene (1/1, D-686); 6, 13. Butyl Acrylate-Styrene (1/1, D-687); and 7, 14. Vinyl Acetate-Styrene (1/1, D-688). Samples for the left half of the chart were degassed once; the others were not. The sample for the left member of each triplet bar-graph was on a 45-minute cycle at 75°C, the center one on a 1/2- to 3-minute cycle at 25°C, and the right one received continuous irradiation at 25°C. Dose rate: 10,000 rads per exposure or 2,500 rads per second. Dose: 50,000 rads.

F. Summary

From these data, on the composite effect of degassing and the irradiation cycle, it is concluded that:

1. Something more than a three-minute cycle, with the parameters used, is required for an optimal yield of polymer at a given dose rate and dose level.

2. The effects of both degassing and the irradiation cycle are dependent to some extent at least on the monomer system.

3. The effect of degassing is more dependent on the monomer system than is the effect of the irradiation cycle.

4. The relative composite effect of degassing and the irradiation cycle decreases in general with an increase in dose rate and total dose.

G. Acknowledgments

The authors express their appreciation for the helpful assistance of: (1) Drs. E. D. Black, H. S. Levinson, C. Merritt, Jr., Charles C. Rainey, and Charles E. Waring for reviewing this report, (2) Mrs. Phyllis Zelezny for her painstaking care in the preparation of the copy for reproduction, (3) W. H. Hall, who built the high vacuum system and prepared the sample tubes, and (4) the Exhibits Branch, the Photographic Section, and the Reproduction Branch for their respective contributions.

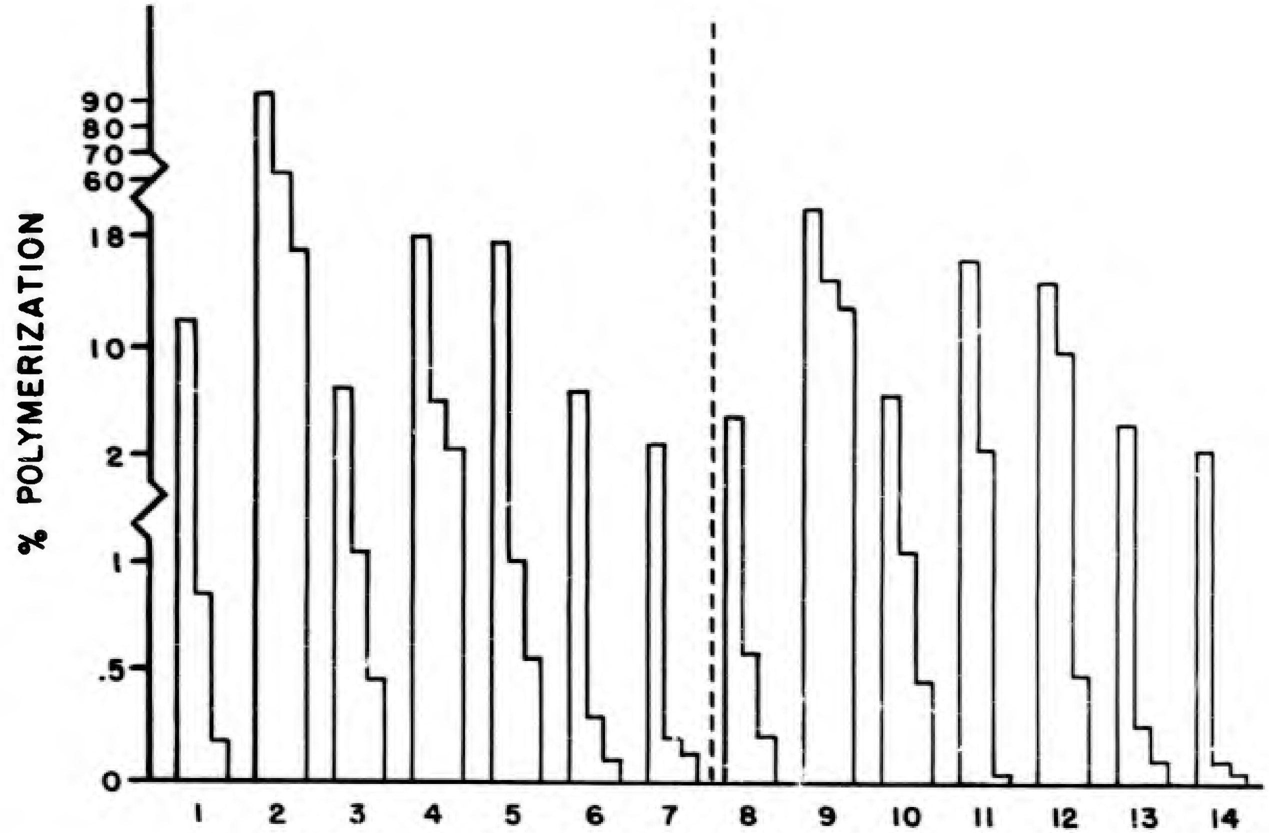

Figure 10. 1, 8. Acrylonitrile (D-682); 2, 9. Butyl Acrylate (D-683); 3, 10. Styrene (D-684); 4, 11. Vinyl Acetate (D-685); 5, 12. Acrylonitrile-Styrene (1/1, D-686); 6, 13. Butyl Acrylate-Styrene (1/1, D-687); and 7, 14. Vinyl Acetate-Styrene (1/1, D-688). Samples for the left half of the chart were degassed once; the others were not. The sample for the left member of each triplet bar-graph was on a 45-minute cycle at 75°C, the center one on a 1/2- to 3-minute cycle at 25°C, and those for the right member were given continuous irradiation at 25°C. Dose rate: 100,000 rads per exposure or 25,000 rads per second. Dose: 500,000 rads.

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